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ON THE UNIMOLECULAR REACTIONS OF CH_3O AND CH_2OH^*

George F. ADAMS

USA ARRADCOM/Ballistics Research Laboratory, Aberdeen Proving Ground, Maryland 21005, USA

and

Rodney J. BARTLETT and George D. PURVIS

Quantum Theory Project, University of Florida, Gainesville, Florida 32611, USA

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Recent experiments suggest that the isomerization reaction $\text{CH}_3\text{O} \rightleftharpoons \text{CH}_2\text{OH}$ may compete with the hydrogen dissociation reaction $\text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} + \text{H}$. We report correlated many-body calculations of barrier heights for these reactions and other decompositions of CH_3O and CH_2OH . The barriers for isomerization and dissociation are similar, while the reaction $\text{CH}_3\text{O} \rightarrow \text{HCO} + \text{H}_2$ has a higher energy barrier.

1. Introduction

The methoxy radical CH_3O is thought to play an important role in hydrocarbon oxidation processes relevant to combustion and photochemical air pollution [1]. Recently, Radford [2] has suggested that the unimolecular isomerization of methoxy to form the hydroxymethylene radical,



followed by the fast reaction



may provide an alternate route for the oxidation of methyl radicals. Subsequently, Batt et al. [3] pointed out that although the isomerization reaction should be competitive with the hydrogen-dissociation reaction of the methoxy radical,



neither reaction should occur quickly enough to com-

pete with other faster reactions of the radical that are important in atmospheric chemistry. However, at the higher temperatures encountered in combustion processes, the unimolecular reactions may be more significant.

Here we report computed classical barriers for several unimolecular reactions of CH_3O and CH_2OH . In addition to (1) and (3), we also discuss the hydrogen-dissociation reactions of hydroxymethylene,



and the hydrogen molecule elimination reaction of methoxy,



2. Outline of the calculations

For each of the open-shell species in this study an unrestricted Hartree-Fock (UHF) wavefunction is chosen for the ground electronic reference state. The structural parameters for the reactants and the various transition states are determined using the analytic gradient based GRADSCF codes [4] and a 6-31G** basis

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[5]. The many-body perturbation theory (MBPT) calculations use double zeta-quality basis sets [6] augmented with polarization functions on all atoms [6]. Since self-consistent-field calculations provide poor estimates of energy differences, the electronic energy is determined using MBPT [7]. In particular, fourth-order MBPT calculations that include all single-, double-, and quadruple excitation diagrams [SDQ MBPT(4)] are reported.

3. Equilibrium configurations for methoxy and hydroxymethylene

The structural parameters determined for the methoxy and hydroxymethylene radicals are shown in fig. 1. Our SCF calculations predict structural parameters for CH_3O that agree closely with those of Yarkony et al. [8]. Each of the SCF calculations, however, disagrees somewhat with the results of our previous correlated D MBPT(4) calculation for this radical [9]. In that study, Bent et al. showed that the C_{3v} symmetry axis is broken by a reduction in the in-plane OCH bond angle, while, to the contrary, the SCF calculations predict that the symmetry changes via an increase of the in-plane OCH bond angle. A correlated calculation of the CH_3O , CH_3OH , CH_2O , and HCO structures has also been published [10]. Since the structures of the radicals and transition states described in this work are determined using UHF calculations, for consistency, all energy differences for the methoxy reactions are computed at the structural parameters determined in the UHF calculations.

The electronic energies for the two radicals, including both the UHF and SDQ MBPT(4) results, are reported in table 1. Interestingly, the UHF calculations suggest that the methoxy radical CH_3O is more stable

Table 1
Electronic energy predictions (hartree)

Structure	UHF	SDQ MBPT(4)
CH_3O , equilibrium	-114.4484	-114.7621
CH_2OH , equilibrium	-114.4419	-114.7684
1,2-shift SP ^{a)}	-114.3668	-114.7054
$\text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} + \text{H SP}$	-114.3845	114.7060
$\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H SP}$	-114.3679	-114.6923

^{a)} SP = saddle point.

than the hydroxymethylene radical CH_2OH . The energy difference equals 4.07 kcal/mole. On the other hand, the correlated SDQ MBPT(4) calculations predict that the hydroxymethylene radical is more stable, by 3.90 kcal/mole. Experimental studies [11,12] indicate that hydroxymethylene is 5–10 kcal/mole more stable than methoxy, although a more recent experimental [13] determination of the heat of formation of the methoxy radical would reduce this range by 3 kcal/mole. Our result of 3.90 is in good agreement with this lower (2–7 kcal/mole) estimate.

4. Isomerization and dissociation reactions

The isomerization reaction that converts methoxy to hydroxymethylene belongs to the reaction class identified as 1,2-hydrogen shifts. A recent review by Schaefer [14] discusses this class of reactions. The transition state identified for the isomerization reaction is shown in fig. 2. Such isomerizations are often ignored in chemical kinetic models, since it is assumed that the potential energy barrier for the reaction is large. As the results in table 1 show, however, the electronic energy for this transition state does not differ significantly from those values calculated for the two hydrogen-dissociation reactions.

In particular, as summarized in table 2, the classical barrier for the isomerization, reaction (1), is 35.6 kcal/mole (39.5 kcal/mole for the reverse reaction) with the competing H-dissociation, reaction (3), having a 35.2 kcal/mole barrier. The UHF transition state structures are shown in fig. 2. Since the 1,2 shift transition state has a more compact structure, one would expect that the zero-point vibrational energy differences would re-

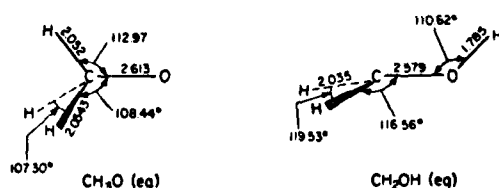


Fig. 1. UHF predicted equilibrium structures for CH_3O and CH_2OH (bond lengths in bohr).

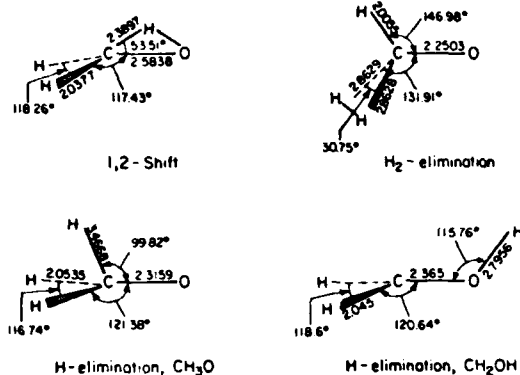


Fig. 2. UHF predictions of transition states for CH_3O undergoing 1,2-H shift, H elimination, H_2 elimination, and for H elimination from CH_2OH (bond lengths in bohr).

sult in a lower 0 K activation barrier for (3) than for (1). Nevertheless, the classical barriers are so nearly equal that it is expected that both reactions will occur under most conditions.

In addition to the above, the H-dissociation reaction, reaction (4), is also of interest. The competing reaction



is ruled out since its energy barrier is greater than 85 kcal/mole [15–17].

The saddle-point structure for (4) is shown in fig. 2. SDQ MBPT(4) calculations at the UHF determined geometries suggests a barrier of 47.8 kcal/mole for (4). Consequently, it would appear that the preferred unimolecular reaction of CH_2OH is the isomerization to CH_3O .

Table 2
Reaction barriers (kcal/mole)

Reaction	Barrier height ^{a)}
$\text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} + \text{H}$	35.2
$\text{CH}_3\text{O} \rightarrow \text{CH}_2\text{OH}$	35.6
$\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{O}$	39.5
$\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}$	47.8

^{a)} All barrier heights are classical. No attempt has been made to correct for differences in the zero-point vibrational energies.

5. The H_2 -elimination reaction of methoxy

The reaction of methoxy to produce the formyl radical and hydrogen molecule is similar to the molecular products reaction channel of formaldehyde [16–22]. Like formaldehyde, the methoxy radical has a hydrogen-dissociation channel, an isomerization channel, and an H_2 -elimination channel. Recent MINDO/3 results suggest that the dominant dissociation of the radical is the H_2 -elimination reaction [23]. Furthermore, those results suggest that the isomerization reaction and the H_2 -elimination reaction have nearly the same activation energy.

We have made numerous efforts to locate the H_2 -elimination reaction saddle point using the GRADSCF computer codes. The structure shown in fig. 2 corresponds to a structure for which the norm of the gradient satisfies a stringent convergence criterion. Proper identification of a saddle point, however, requires the calculation of the vibrational frequencies for the structure. If one of the vibrational frequencies is imaginary, then the structure corresponds to a saddle point. The structure shown in fig. 2 fails this test, because the vibrational analysis yields two imaginary frequencies. Additional study of the hypersurface in this region, however, suggests that the second imaginary frequency is due to an artifact in the SCF results for this structure. In particular, our UHF wavefunction breaks the C_s symmetry assumed for the problem. The symmetry breaking may be viewed as due to the existence of a large-amplitude wagging motion characterized by a double-minimum potential energy function. This vibration may be viewed as a rocking of the H_2 fragment perpendicular to the plane defined by the formyl radical fragment.

To test this view, we extended the "transition state" along the apparent reaction coordinate, and searched for a minimum on the hypersurface. This calculation leads to a minimum that corresponds to the products H_2 and HCO . Distortion of the structure along the normal mode of the second imaginary frequency followed by steepest-descent minimization appears to lead to no products. Instead, the search routine wanders in hyperspace near the transition state structure. After twelve evaluations, the structure remains almost equivalent to that located by the transition state search routine.

Finally, to test whether the symmetry breaking was an artifact of the UHF calculation, a transition-state search was carried out using an analytic gradient based

restricted Hartree-Fock calculation. This calculation also converged, in forty-eight function evaluations, to a structure with no plane of symmetry. The bond lengths and bond angles predicted in that calculation are close to those predicted by the UHF calculations. Furthermore, when force constants for the structure are calculated at the RHF level, we still obtain two imaginary frequencies. Thus there is no substantial difference between the UHF and RHF predictions.

In sum, our calculations to date demonstrate that the transition state does lead to the hydrogen molecule product. The calculations do not conclusively demonstrate the existence of a double-minimum potential well about the transition state. To determine whether this potential is, as we believe, an artifact of the SCF level calculations requires a re-examination of this transition-state region using a theoretical method that includes correlation effects. We anticipate reporting such calculations soon.

The electronic energy including the correlation energy for this transition state is -114.6732 au, and the reaction barrier, 55.8 kcal/mole, can be compared with the other reaction barriers in table 2. The barrier for the H_2 -elimination reaction exceeds the barriers determined for the other methoxy radical reactions by more than 20 kcal/mole.

6. Discussion and conclusion

The energy barrier results determined by these calculations and summarized in table 2 support Radford's contention that the hydrogen-dissociation and isomerization reactions of methoxy radical could compete favorably under appropriate conditions. In addition, these results suggest that for hydroxymethylene, the isomerization reaction should be faster than the hydrogen-dissociation reaction. Finally, our preliminary results indicate that the H_2 -elimination reaction of the methoxy radical has a much larger energy barrier than either of the other methoxy reactions considered here. In all cases, the calculations do not consider the sometimes important effect of the fourth-order triplet-excitation diagrams [22,24,25] and are limited to UHF determined structures. For example, the triple-excitation contribution in $H_2CO \rightarrow H_2 + CO$ reduced the barrier by ≈ 3 kcal/mole [22] and it is possible to obtain similar changes by using better, correlated structures. The spin contamination present in UHF calculations

can sometimes cause additional problems. For the H_2 -elimination pathway, the UHF multiplicity is 2.013 and SDQ MBPT(4) improves this. We expect that a correlated determination of the (5) transition state should eliminate any possible artifacts with the SCF transition state.

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